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Short communication

Nanomechanical characterization and mechanical integrity of unaged and aged Li-ion battery cathodes

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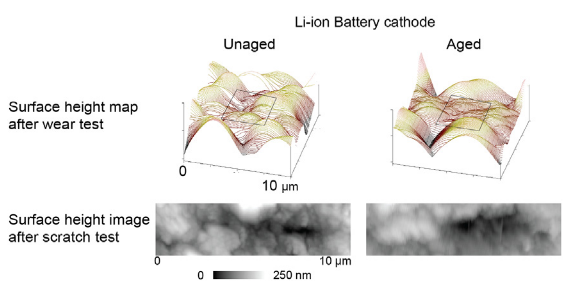
HIGHLIGHTS

- Nanomechanical and mechanical integrity tests conducted on Li-ion battery cathodes.
- The aged cathode showed higher hardness, creep depth and critical load in scratch.
- The aged cathode shows lower wear depth and coefficient of friction.
- The aged cathode showed high creep behavior, suggesting PVDF binder degradation.
- High hardness in the aged cathode, believed to make it brittle, seen in scratch test.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-ion (Li-ion) batteries have been implemented for numerous applications, one of which is in plug-in hybrid electric vehicles (PHEV) and pure electric vehicles (EV). In an effort to prolong battery life it is important to understand the mechanisms that cause reduced battery capacity with aging. In this work, nanomechanical characterization and mechanical integrity studies were carried out on unaged and aged $LiFePO_4$ battery cathodes using atomic force microscopy (AFM) and nanoindentation. Changes in hardness, elastic modulus, creep, nanowear, nanoscratch and nanofriction properties were measured. Measured changes are believed to occur as a result of coarsening and agglomeration of $LiFePO_4$ nanoparticles.

1. Introduction

Reliance on battery technology has drastically increased as there is a need for portability in performing daily activities. This need for greater portability requires greater storage capacity with compact sizes. A battery is a device that stores chemical energy and converts it to electrical energy when needed. Battery types vary with chemistries and shape, some of which are lead-acid, nickel-cadmium, nickel-metal hydride and lithium-ion (Li-ion). Li-ion batteries have been identified to provide high specific energy. Li-ion battery usage rapidly expanded with numerous applications in portable electronics, power tools and transportation. In the transportation industry batteries are needed in order to reduce reliance on oil and to yield more environmentally friendly vehicles [13,14,18].

Lithium iron phosphate ($LiFePO_4$), which was first introduced in 1997 [20], was found to be a good choice for cathode material. The $LiFePO_4$ cathode has been studied extensively because of its high specific capacity (on the order of 170 mAh g^{-1}), high thermal

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stability, high specific energy (on the order 0.60 Wh g^{-1}) as well as low cost and low toxicity [6,8,22]. $LiFePO_4$ is considered one of the best options in achieving the United States Advance Battery Consortium (USABC) goals for EVs and PHEVs [1–3].

During the operation of a Li-ion battery, charge and discharge cycles reduce its capacity and power. It is therefore important to study the cause of these aging mechanisms in order to increase the life of the battery. One such mechanism was found to be coarsening of $LiFePO_4$ particles in aged cathodes by particle agglomeration as shown in Fig. 1 [15,21]. The agglomerated particles are believed to consist of small particles produced by the break up and/or formation of nanocrystalline deposits. Particle sizes for unaged cathodes were between 150 and 250 nm, while larger agglomerated particles for the aged were in the range of 350–400 nm which consisted of smaller particles of sizes ranging from 100 to 150 nm. Coarsening of nanoparticles has been shown to lead to an increase in surface resistance and decrease in surface conductivity, which is responsible for reduced lithium retaining capacity.

Wang [24] observed crack propagation in $LiFePO_4$ cathode material after cycling using a scanning electron microscope. This was stated as a result of high internal strain during lithiation and delithiation in the cathode particles. A volume change of approximately 7% was observed by Meethong et al. [12] to occur during lithiation and delithiation while the chemistry of nanoparticles change between $LiFePO_4$ and $FePO_4$ phases.

Simulations of intercalation stresses carried out by Christensen and Newman [9] and Zhang et al. [23] on $LiMn_2O_4$ battery electrode particles showed that larger particles produced larger stresses during intercalation. Based on a study of the effect of stress accumulation within the $LiFePO_4$ cathode, Huang and Wang [11] reported that dislocations and distortion zones were formed through phase transformation of $LiFePO_4$ particle during lithiation and delithiation. It was suggested that this formation and movement of dislocation would lead to crack formation in the cathode. The high internal stresses created during charge and discharge can lead to change in nanomechanical properties and degradation of mechanical integrity of the cathode.

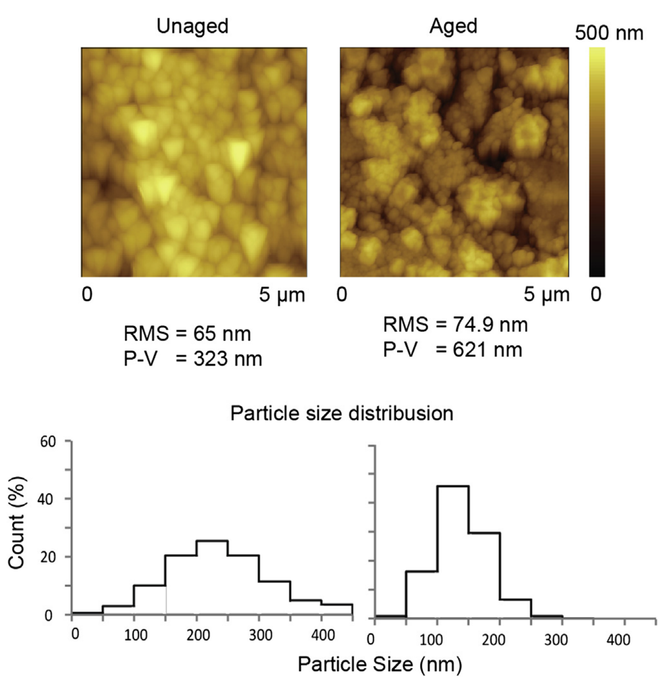

Fig. 1. AFM Surface height images with RMS and P–V distance values and particle distributions of unaged and aged $LiFePO_4$ cathode samples. (Adopted from Ramdon and Bhushan [21]).

It is of interest to conduct nanomechanical characterization to examine properties such as hardness (H), elastic modulus (E) and creep. Studying hardness is a measure of the cathodes' plastic deformation property while elastic modulus gives the information about elastic deformation. Creep provides information about the viscoelastic nature of the cathode. Mechanical integrity can be studied by performing various durability experiments which include nanowear, nanoscratch and nanofriction experiments [4,5]. The Nanowear experiment can simulate repeated loading and unloading of the cathode. Conducting nanoscratch investigation will allow studying the failure mechanism of the cathode. Scratch resistance can be obtained by observing the changes in friction. It is also important to examine friction on the nanoscale as this can be used as an indicator to the change in the mechanical properties of the cathode [4,5].

In this work, nanomechanical characterization and mechanical integrity studies were carried out on unaged and aged $LiFePO_4$ battery cathodes using an AFM and nanoindentor. To conduct nanomechanical characterization, hardness (H), elastic modulus (E) and creep experiments were performed. For mechanical integrity studies, nanowear, nanoscratch and nanofriction experiments were performed.

2. Experimental details

2.1. Li-ion battery samples

Cylindrical Li-ion cells used in the experiments have cathode material on an aluminum current collector made of $LiFePO_4$ nanoparticles with polyvinylidene fluoride (PVDF) binder and carbon coating added for increased conduction. Graphite on a copper current collector is used as the anode and lithium hexafluorophosphate ($LiPF_6$) salt in alkaline carbonate solvent as the electrolyte. The anode and cathode are separated by a separator and are rolled in a tube to create the cell. The cell has an operating voltage of 3.3 V and a nominal discharge capacity of 2.3 Ah.

Two identical commercial cells were selected, one termed unaged and the other aged. The unaged cell was charged and discharged completely at 1C (1C = 2.3 Ah) to verify its capacity. The aged cell was cycled until end of life (EOL) was reached. This is defined according to the automobile industry as when the cell's capacity is reduced by 20% [3]. The aged cell was cycled at a C-rate of 7C, between 60 and 75% state of charge (SoC) and at 45 °C [17]. The C-rate is a unit that is used to measure the charge and discharge currents of a battery. A charge rate of 7C means it would take 1/7 h to charge and 1/7 h to discharge if it is discharged at a current of 7 (2.3) = 16.1 A. SoC range represents the level at which the battery is charged then discharged to complete a cycle. The lifespan of the battery will depend on the rates at which the battery is charged and discharged, the state of charge region and temperature in which the battery was operated. The cells were then discharged completely and disassembled in a glove box filled with Argon atmosphere with dew point of about −34 °C. The $LiFePO_4$ cathode samples used in this study were then taken from the unaged and aged cells and sections close to the center of the cell were chosen because the center was shown by thermal diffusivity to have greater signs of aging [16].

2.2. Nanomechanical characterization

The hardness and elastic modulus of the cathode samples were measured using a probe based scanning nanoindenter head (TS 75 Triboscope, Hysitron, Inc.) which was attached to an AFM (Bruker

Dimension 3100, Santa Barbara, CA) with a diamond Bercovich tip (~ 100 nm radius). Nanoindentations were conducted in displacement control mode and a maximum indentation depth of 1000 nm was used for each indent. This depth was chosen to allow sufficient penetration into the cathode to avoid surface roughness effect in the hardness measurement. Nanoindentation depth as a function of time schematic of the experiment is shown in Fig. 2 (top). The load was ramped until the depth of 1000 nm in 10 s was reached and then the surface was unloaded in 10 s. A minimum of 20 nanoindentations were performed at different locations and the hardness (H) and elastic modulus (E) were calculated using the Oliver and Pharr method [19]. The average value of hardness and elastic modulus were then calculated along with standard deviation.

Creep tests were performed using load control where a constant load of 1000 μN was applied for 60 s using the nanoindentor with a diamond Bercovich tip (~ 100 nm radius). The load was chosen to provide enough penetration depth into the cathode. A minimum of six creep experiments were carried out on both samples at different locations and the average creep from each sample was calculated. The average creep depth was calculated by averaging the difference in indentation depth at the beginning and end of the constant load applied among the six experiments for each sample. Load as a function of time is shown in Fig. 3 (top).

2.3. Mechanical integrity studies

Nanowear, nanofriction and nanoscratch experiments were performed using the probe based scanning nanoindentor previously described. In nanowear experiment a 5 μm diamond conical tip (60° cone angle) was used. During nanowear a scanning speed of 2 μm s^{-1} was used and an area of 5 μm × 5 μm was scanned. Cathode surfaces of 10 μm × 10 μm were scanned before and after the wear experiment at a scanning speed of 0.7 μm s^{-1} such that initial and final surface topography of the wear region as well as surrounding areas were obtained. Loads used were 50 and 100 μN for 1 wear cycle for each sample. Average height decrease of worn area was measured as average wear depth of worn area.

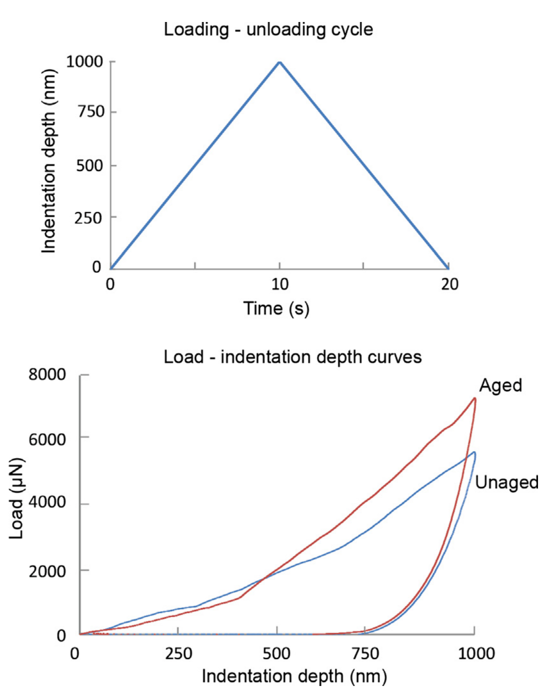

Fig. 2. Indentation depth as a function of time for hardness and elastic modulus experiment and load as a function of indentation depth for unaged and aged cathode samples.

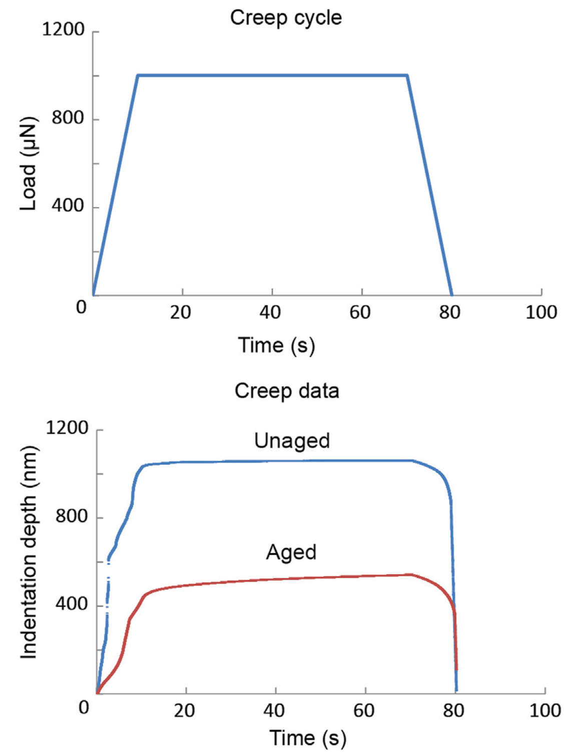

Fig. 3. Load as a function of time for indentation creep experiment and indentation depth as a function of time for unaged and aged cathode samples.

A 20 μm diamond conical tip (90° cone angle) was used for the nanoscratch experiment. Scratch was performed with the increase in applied normal load from 0 μN to 350 μN through a scratch length of 10 μm for 10 s. An AFM image of the surface was taken before and after the scratch at a scan speed of 1 Hz. The coefficient of friction at each point was calculated by dividing the friction force by the normal load. The coefficient of friction as a function of normal load was then plotted to determine the critical load of the surface, at which the coefficient of friction increases rapidly [5].

Nanofriction experiments were carried out using a 20 μm diamond conical tip (90° cone angle). The experiments were performed in the load range of 50–300 μN for 10 μm scratch length with a scratch speed of 1 μm s^{-1}. These experiments were performed five times at different surface locations for each load. The average friction force as a function of load was plotted for each sample. The coefficient of friction was obtained as the slope of friction force versus applied normal load curve.

All measurements in this study were obtained under the same ambient atmosphere (22 ± 1 °C and 45 ± 5% RH).

3. Results and discussion

Nanomechanical characterization and mechanical integrity studies of unaged and aged $LiFePO_4$ battery cathodes were performed, and results of hardness, elastic modulus, creep, nanowear, nanoscratch and nanofriction are presented in this section.

3.1. Nanomechanical characterization

Nanomechanical properties of the unaged and aged cathodes were measured using nanoindentation technique. Measured hardness and

Table 1
Nanomechanical and friction properties of unaged and aged cathodes.

Properties	Unaged	Aged
H (MPa)	64 ± 7	124 ± 17
E (GPa)	4 ± 0.5	4.1 ± 0.4
Av. creep depth in 60 s (nm)	14 ± 2	49 ± 3
Wear depth – 50 μN (nm)	478 ± 32	109 ± 19
Wear depth – 100 μN (nm)	906 ± 43	131 ± 21
Critical load in scratch (μN)	120 ± 9	175 ± 12
Coefficient of friction	0.42 ± 0.02	0.30 ± 0.02

elastic modulus of the cathode were measured from the load as a function of indentation depth curve as shown in Fig. 2 (bottom). The average hardness and elastic modulus obtained for the unaged and aged cathodes are reported in Table 1. The unaged cathode has a hardness of 64 MPa and the hardness of the aged was found to be 124 MPa. As discussed in the introduction section, the high internal stress and strain created in $LiFePO_4$ cathode during lithiation and delithiation are believed to form dislocations which may lead to the hardening of the cathode. The elastic modulus of both unaged and aged cathodes is about the same when the measurement error was considered.

In order to understand the creep behavior of the cathode, a 1000 μN load for 60 s indentation on unaged and aged cathodes were performed. The resulting indentation depth as a function of time are presented in Fig. 3 (bottom) for unaged and aged cathodes. Indentation depth increases on average 13 nm with the unaged cathode (Table 1) and the aged cathode increase on average by 49 nm. This data suggested that the aged cathode shows high creep behavior while unaged cathode shows low creep behavior. Hackney et al. [10] studied creep behavior of Sn-C/PVDF composite anode for Li-ion batteries using the nanoindentation method and reported that creep occurs, which was used as a measure of failure of the composite structure. For the $LiFePO_4$ cathode, the creep could occur due to the change in the viscoelastic properties of the PVDF binder as the cathode ages. This would suggest evidence of binder degradation occurring in the cathode.

3.2. Nanowear experiments

Nanowear experiments were performed on unaged and aged cathodes at 50 and 100 μN loads. The average height decrease of worn area was measured as the average wear depth of worn area. Wear of a 5 μm × 5 μm of unaged and aged cathodes are shown in Fig. 4 for both 50 μN and 100 μN load. It can be observed that the unaged surface showed greater wear of the cathode than the aged. Table 1 shows the average wear depth that was obtained. For 50 μN load the average wear for the aged cathode is 109 nm and for the unaged 476 nm. The degree of wear in the aged cathode is 77.5% less than that of unaged cathode. At 100 μN load the average wear depth for unaged cathode is 906 nm and for aged is 131 nm, equivalent to 85% reduction in wear for aged cathode. The hardness of the aged cathode is 48% greater than that of the unaged and this is reflected in the nanowear results.

For the aged cathode in Fig. 4 a flattening effect can be seen where the particles that were asperities are now more compressed into the substructure of the cathode. The unaged cathode observed from the particle behavior after wear was more easily plowed and rearranged when compared to the aged cathode. Significant plowing was observed for the unaged cathode under 150 μN load. The particle

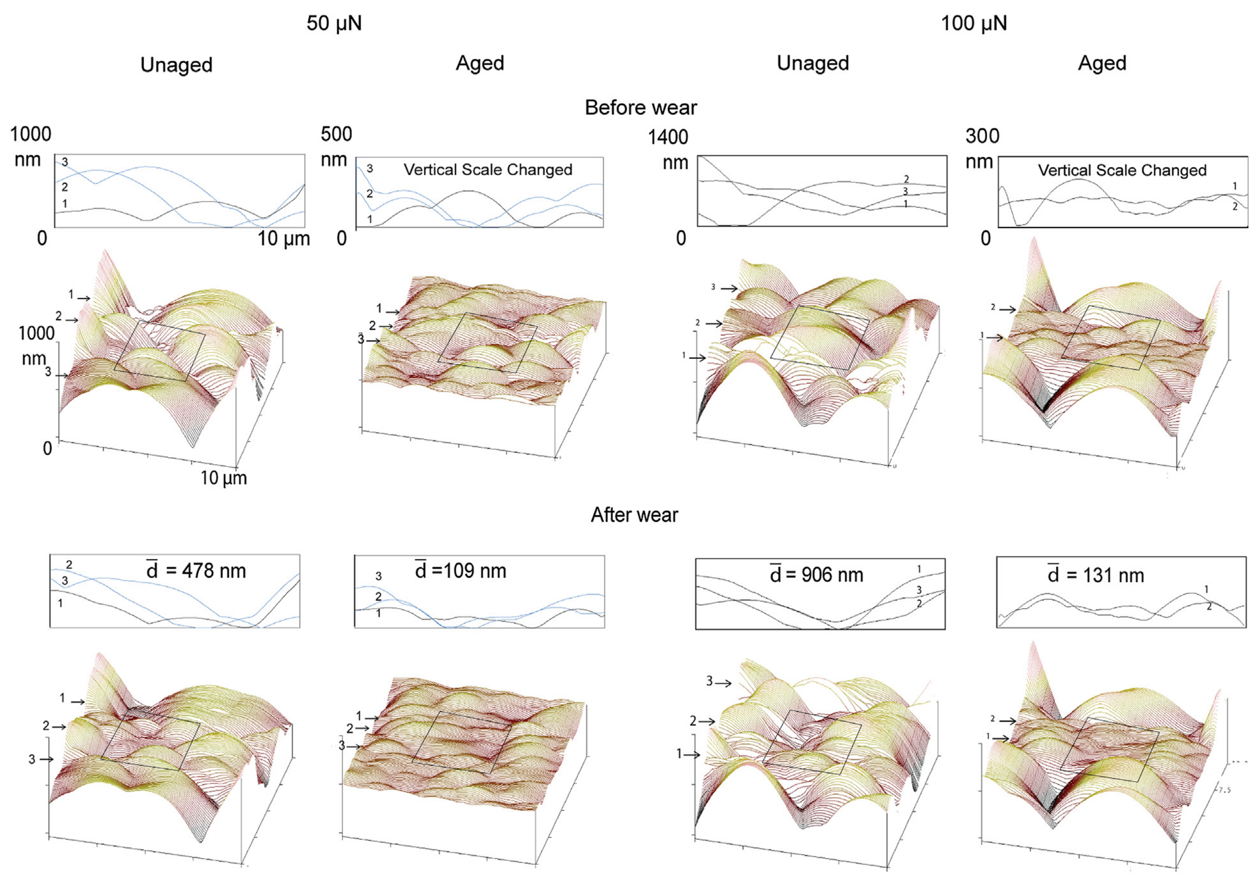

Fig. 4. Surface height maps and sections of unaged and aged cathodes showing worn region at 50 μN and 100 μN loads. Average wear depth ($\bar{d}$) are listed in the sections.

with uniform asperity was plowed through the center and the after line map showed a valley created. When comparing the effect of doubling the load on both the unaged and aged cathodes, the unaged cathode responded with a 90% increase in the wear depth whereas for the aged cathode wear depth only increased by 20%. This is believed to be due to higher hardness of the aged cathode.

3.3. Nanoscratch experiments

Nanoscratch experiments were conducted to determine the failure mechanisms present in the unaged and aged cathodes. Fig. 5 shows nanoscratch results obtained for unaged and aged cathodes and nanoscratch on silicon for reference. The coefficient of friction as a function of normal load was plotted. At low load coefficient of friction was constant, at a certain load the coefficient of friction increased rapidly. The load at which this rapid increase in coefficient of friction occurs is known as the critical load [5]. The critical load shows the load at which the surface of the cathode yields and plastic deformation occurs. The critical loads for unaged and aged are 120 and 175 μN, respectively (Table 1). The arrows in the height images show visible damage to the cathodes which occur as a result of plastic deformation and fracture. The aged cathode appears to be more scratch resistant than the unaged due to the higher hardness. However, the aged cathode breaks up catastrophically which appear to be in a brittle mode at loads higher than 175 μN.

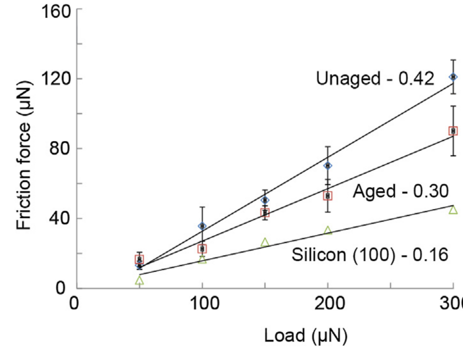

Fig. 6. Coefficient of friction as a function of normal load and height images of unaged and aged cathodes and silicon (100) sample for reference. Arrow in height images of scratched surfaces indicates damaged regions.

Nanoindentation and nanowear experiments were performed by Chen et al. [7] on Ni–Sn alloy coating for Li-ion battery study. Crack formation was observed during wear experiment and these were proposed to be similar observation of surface damage to that of anode during charge-discharge cycling. The sliding contact stresses were proposed to be similar to the stresses due to the phase change of the anode during charge–discharge cycling.

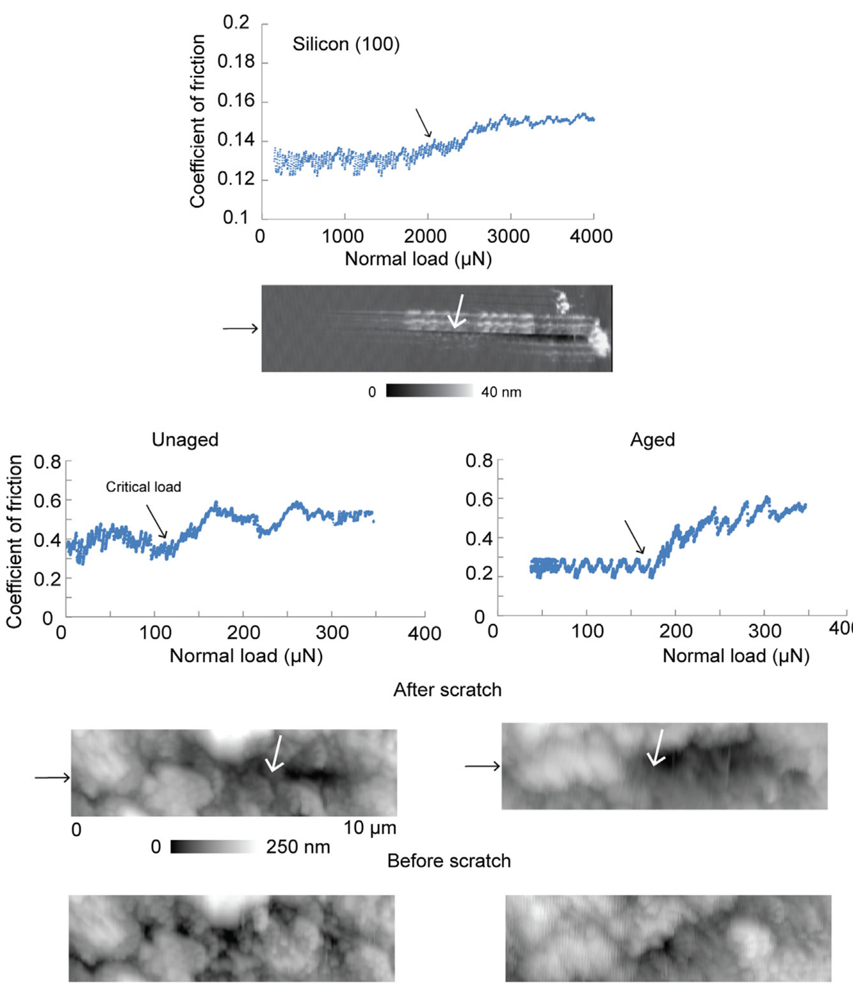

Fig. 5. Friction force as a function of load for unaged and aged cathodes and silicon (100) for reference. Coefficient of friction values obtained from the slope of the curves are also presented.

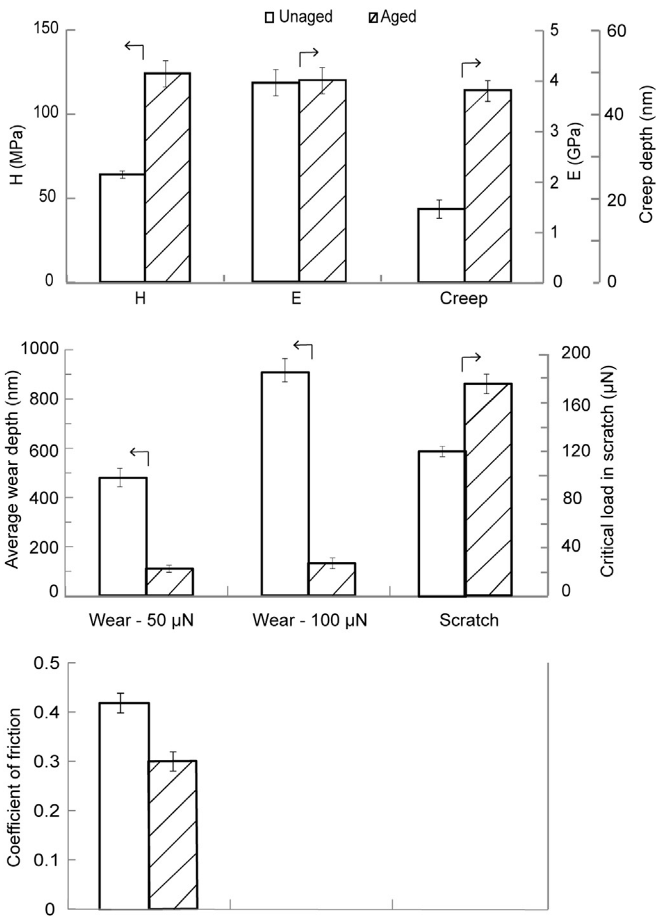

Fig. 7. Bar chart showing hardness (H), elastic modulus (E), average creep depth, average wear depth at 50 μN and 100 μN loads, critical load in scratch and coefficient of friction of unaged and aged cathodes.

3.4. Nanofriction experiments

The nanofriction experiments conducted (Fig. 6) show that friction force of unaged and aged cathodes increased linearly with applied load. At any given load the friction force of the unaged was higher than the aged. The coefficient of friction was measured as the slope of the friction force versus applied normal load. The coefficient of friction values are shown in Table 1 and Fig. 6. The coefficient of friction for the unaged cathode is found to be 0.42 and for the aged cathode 0.30. This is due to the higher hardness of the aged cathode.

4. Conclusions

Coarsening and agglomeration of $LiFePO_4$ nanoparticles have been observed during aging, which is expected to increase residual stresses within the cathode. Nanomechanical characterization and mechanical integrity studies were carried out to determine the effect of change in physical and chemical properties and the increase in internal stresses during aging. Measured nanomechanical properties include hardness, elastic modulus, and creep, while mechanical integrity properties include of unaged and aged $LiFePO_4$ battery cathodes nanowear, nanoscratch and nanofriction. Data are summarized in Fig. 7. The aged cathodes shows higher hardness, creep depth and critical load in scratch and lower wear depth and coefficient of friction. Higher hardness in the aged cathodes is believed to make it brittle and during scratch test, catastrophic damage is observed. Increase in creep depth is believed to be due to the binder degradation during aging.

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